



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP96/03098 <b>(22) International Filing Date:</b> 9 July 1996 (09.07.96)  <b>(30) Priority Data:</b> 95304801.4 10 July 1995 (10.07.95) EP <b>(34) Countries for which the regional or international application was filed:</b> DE et al.  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> VERDUIJN, Johannes, Petrus [NL/BE]; Vlieguit 28, B-3061 Leefdaal (BE).  <b>(74) Agents:</b> WHITE, Nicholas, John et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		<b>(81) Designated States:</b> AU, BR, CA, CN, IL, JP, KR, MX, SG, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ZEOLITES AND PROCESSES FOR THEIR MANUFACTURE  <b>(57) Abstract</b>  Colloidal zeolites are prepared from synthesis mixtures in which the silicon source is not completely soluble.		

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"Zeolites and Processes for their Manufacture"

This invention relates to zeolites, and to processes for their manufacture. More especially, it relates to the manufacture of colloidal zeolites, i.e., zeolites with a particle size of at most about 100 nm.

In International Application WO 93/08125, there is described a process for the manufacture of colloidal zeolites. In this process, a boiling aqueous synthesis mixture is prepared, the mixture comprising a source of silica and a basic organic structure directing agent in a proportion sufficient to cause substantially complete dissolution of the silica source. The synthesis mixture is then maintained at an elevated temperature, but at 120°C or lower, for a time sufficient to cause crystals of the desired zeolite, which may, for example, be an MFI, MEL or \*BEA zeolite, to form. The synthesis mixture may also comprise sources of other zeolite components, most importantly of aluminium and an alkali metal. It is stated to be an essential feature that the silica is dissolved in the synthesis mixture at the boiling temperature, this being achieved by the organic base that is also the structure directing agent or template together with an inorganic base, e.g, sodium hydroxide.

Products of particle size at most 100 nm have advantages over larger particle size products, for

example, when used as a catalyst, e.g., in hydrocarbon conversions, they have an enhanced ratio of surface area to mass, high diffusion rates, reactivities and resistance to deactivation by pore plugging and surface contamination. Similarly, they have advantages in organic separations, and are also valuable in the manufacture of supported layers, especially membranes, as described in WO 94/25151, the disclosure of which is incorporated by reference herein. In certain of the procedures described in that International application, the zeolite layer is deposited from a colloidal suspension onto a support; instability in the suspension is deleterious. Accordingly, it would be desirable to have a wider range of processes by which various zeolites capable of forming a stable suspension might be manufactured, and for this purpose a particle size of at most 100 nm is desirable.

It has now surprisingly been found that even in the absence of the inorganic base, or in the presence of insufficient inorganic base to effect complete dissolution of the silica source in the boiling synthesis mixture, colloidal zeolite crystals may be obtained. The procedure allows the formation of a colloidal zeolite suspension with an enhanced zeolite content.

The present invention accordingly provides a process for preparing a zeolite having a particle size of at most

100 nm, which comprises preparing an aqueous synthesis mixture comprising a source of silicon and a basic organic structure directing agent in a synthesis mixture insufficiently alkaline to cause substantially complete dissolution of the silica or in a synthesis mixture containing another reactant essential to the formation of the zeolite which reactant inhibits dissolution of the silica, and hydrothermally treating the synthesis mixture at a temperature below 120°C for a time sufficient to effect formation of the zeolite.

The process is applicable to any zeolite which may be prepared using a source of silica and an organic structure directing agent, for example, MFI, MEL, \*BEA or OFF, e.g., ZSM-5 and other high silica MFI zeolites.

The structure directing agent may be, for example, the hydroxide or a salt of tetramethylammonium (TMA), tetraethylammonium (TEA), triethylmethylammonium (TEMA), tetrapropylammonium (TPA), tetrabutylammonium (TBA), tetrabutylphosphonium (TBP), trimethylbenzylammonium (TMBA), trimethylcetylammmonium (TMCA), trimethylneopentylammonium (TMNA), triphenylbenzylphosphonium (TPBP), bispyrrolidinium (BP), ethylpyridinium (EP), diethylpiperidinium (DEPP) or a substituted azoniabicyclooctane, e.g., methyl or ethyl substituted quinuclidine or 1,4-diazoniabicyclo(2,2,2)octane.

Preferred structure directing agents are the hydroxides of TMA, TEA, TPA and TBA.

Advantageously, the synthesis mixture contains an excess of organic structure directing agent over that necessary to provide template for all the zeolite formed, that is to say, more than previously described in prior art procedures for preparing the same zeolite.

The zeolite produced by the process of the invention is primarily a silicate or an aluminosilicate, and will be described herein as such. It is, however, within the scope of the invention to replace aluminium wholly or partly with gallium, and partly with boron, iron or other trivalent elements, and silicon may similarly be replaced by germanium or phosphorus. It is also within the scope of the invention to include inorganic cations, for example, potassium or sodium, in the synthesis mixture. For MFI, MEL and \*BEA, it is preferred not to add such inorganic cations.

The sources of the various elements required in the final product may be any of those in commercial use or described in the literature, as may the preparation of the synthesis mixture.

For example, the source of silicon may be, for example, silica or silicic acid powder, a silicate, e.g., an alkali metal silicate, or a tetraalkyl orthosilicate.

The source of aluminium if present may be, for example, aluminium metal, e.g., in the form of chips, hydrated alumina, a water-soluble aluminium salt, e.g., aluminium sulphate, or an alkoxide, e.g., aluminium isopropoxide. It has been observed that, while in a synthesis mixture that does not contain certain components, e.g., aluminium or gallium sources, a given quantity of alkali is sufficient to dissolve a given quantity of silica, that quantity of silica will not dissolve in the alkali in the presence of such components. In certain cases, no reasonable quantity of alkali will dissolve the silica in their presence.

Accordingly, while such components are essential for making the zeolite in question, they create processing difficulties by their presence; these difficulties are circumvented by the process of the present invention.

The alkali metal ion source if present is advantageously sodium or potassium hydroxide.

The crystal size may be varied by varying the crystallization temperature, the lower the temperature the smaller the particle size. Advantageously, the temperature is within the range of from 40°C to 97°C, more advantageously from 40°C to 95°C. Temperatures within the range of 45°C to 85°C are preferred. For zeolites containing a source of alumina, the particle size may also be varied by varying the amount of alumina present. However, the effect of varying the amount of

alumina varies from zeolite to zeolite. For example, it appears that increasing the alumina content of a synthesis mixture for an MFI-type zeolite results in an increase in crystal size. On the other hand, increasing the alumina content of a synthesis mixture for producing a zeolite \*BEA results in a decrease in crystal size. Thus for a particular composition of synthesis mixture, i.e. one containing specified amounts of synthesis ingredients, the particle size may be selected quite accurately by selecting an appropriate crystallization temperature.

Hydrothermal treatment may take place for several hours to several weeks.

The second aspect of the present invention is based on the observation that if the concentration of inorganic cations, especially potassium, in the synthesis mixture is reduced from that typically previously used in Offretite synthesis a colloidal suspension of Offretite may be obtained. It has also been found that it is not in fact essential for the synthesis mixture to be clear and homogeneous, as previously suggested, e.g., in WO 93/08125, in connexion with, e.g., MFI production, as necessary for colloidal zeolite production. WO 94/05597 also indicates that though a clear synthesis mixture is a necessary condition for the manufacture of colloidal zeolites it is not a sufficient one. Surprisingly, a mixture in which, for example, the source of silicon is



incompletely dissolved, is capable of yielding uniform colloidal-size Offretite crystals.

The present invention accordingly also provides a process for the manufacture of a colloidal suspension of Offretite, wherein a synthesis mixture having a molar composition, when calculated in terms of oxides, in the following ranges:

$K_2O:Al_2O_3$  0.25 to 0.5:1

$(TMA)_2O:Al_2O_3$  at least 2.0:1

$SiO_2:Al_2O_3$  8 to 10:1

$H_2O:Al_2O_3$  80 to 100:1

wherein TMA represents the tetramethylammonium cation, is subjected to hydrothermal treatment at a temperature and for a time sufficient to form a colloidal suspension of Offretite.

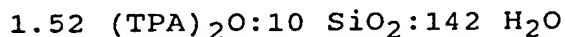
The process of the invention provides individual crystals or agglomerates, and the suspension produced directly, or by washing, is a stable one.

The products of the invention have utility as seeds, or as catalysts, catalyst supports and sorbents, either in layer or particulate form, if desired or required after washing, cation exchange, and/or calcining, in organic reactions and separations.

The following examples illustrate the invention:

Example 1

Silicic acid powder was mixed with an aqueous TPAOH solution (20 wt% in water) and heated. The molar composition of the resulting synthesis mixture was:

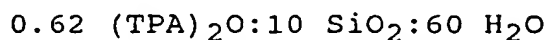


The synthesis mixture was hazy, and was separated into a clear liquid and solid by centrifuging for 20 minutes at 3500 rpm. The clear liquid was decanted through a 0.45  $\mu\text{m}$  filter into a plastic beaker. The whitish gel-like mass remaining on the bottom of the centrifuge vessel was transferred to another plastic beaker, and both beakers were placed in an oil bath at 80°C. After 24 hours, the appearance of the clear liquid had changed from water white to bluish, indicating zeolite formation; the beaker was removed from the oil bath. The appearance of the gel had not changed after 24 hours but after 4.5 days it was observed that the original gelly mass showed colloidal appearance and the gelly character had totally disappeared; this beaker was then removed from the oil bath.

The slurries from the two beakers were each washed with water to pH 10 and dried for several hours at 105°C. X-ray diffraction (XRD) showed that both products were excellently crystalline MFI while scanning electron microscopy (SEM) showed that both products had a mean crystallite size of 60 nm.

Example 2

111.14 g of 20 wt% TPAOH in water (Fluka) were placed in the bowl of a mixer and 59.22 g of silicic acid powder (Akzo SM 604) were slowly added portion-wise with stirring. After the last portion of silica was added a whitish mass with a viscosity like that of heavy syrup resulted. The molar composition was



the molar ratio of TPAOH/SiO<sub>2</sub> being about 0.12.

The synthesis mixture was transferred to a 250 ml plastic flask, which was placed in an oil bath at 50°C with the flask connected to a reflux condenser. The appearance of the synthesis mixture was monitored. For 25 days' heating no change was observed, whereas after 27 days a bluish hue appeared and the viscosity changed from that of heavy syrup to water-like. The observation showed that although at this temperature the onset of crystallization is delayed crystallization is rapid once it starts.

The product was washed to a pH of 10.6, and a portion of the washed slurry evaporated to dryness in a 120°C oven, it being calculated that the solids content of the slurry was 26.6%. The dried product was calcined for 18 hours at 500°C, with a weight loss of 13.3%. From this result, it appeared that the yield on silica was 91%. The washed slurry was allowed to stand for 8 days, no sedimentation being observed after this period.

XRD showed an excellently crystalline MFI product while SEM showed that the solids consisted of spherical particles with a diameter of about 80 nm.

In a comparative experiment, a substantially identical synthesis mixture was placed in an autoclave and maintained at 120°C for 96 hours. The product was also pure MFI, but consisted of spherical particles of 700 nm diameter.

### Example 3

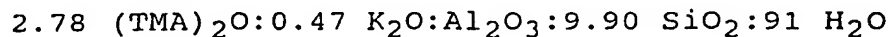
Colloidal Offretite of particle size below 50 nm was prepared from a synthesis mixture containing the following components:

#### Parts by Weight

TMAOH, 25% by weight in water (Fluka)	108.52
Al chips, 99.99% wt purity (Fluka)	2.8924
SiO <sub>2</sub> powder, 89.8% wt, 10.2% water (Baker)	35.52

(It is believed that a small proportion of KOH was present as contaminant in the TMAOH.)

The Al chips were dissolved in the TMAOH solution with stirring and gentle heat. After addition of the silica powder, the mixture was heated to boiling with stirring and kept at boiling point for 5 minutes. It was apparent that not all the silica had dissolved, some settling on the base of the glass beaker. The molar composition of the synthesis mixture was:



The synthesis mixture was homogenized by vigorous stirring for several minutes, then immediately poured into a plastic bottle which was placed in an oil bath, the open end of the bottle being connected to a reflux condenser. The oil bath was heated to 85°C, and maintained at that temperature over a period. The appearance of the mixture gradually changed, with the quantity of deposited silica reducing, while the mixture developed into a transparent jelly. Heating was terminated after 160 hours.

After washing using a 17500 rpm centrifuge, the product was suspended in the last wash water, a stable, colloidal, suspension resulting. A portion was evaporated to dryness and characterized by XRD and SEM. Although the diffractogram showed weak and broad peaks, the pattern was still recognizable as pure Offretite. The SEM showed that the product consisted of uniformly sized and shaped particles, about 45 nm x 20 nm. XRD analysis of a portion of product calcined in air at 475°C for 20 hours showed essentially no change in crystallinity, evidence of thermal stability.

CLAIMS:

1. A process for preparing a zeolite having a particle size of at most 100 nm, which comprises preparing an aqueous synthesis mixture comprising a source of silicon and a basic organic structure directing agent in a synthesis mixture insufficiently alkaline to cause substantially complete dissolution of the silicon source in the synthesis mixture or containing another reactant essential to the formation of the zeolite which reactant inhibits dissolution of the silica, and hydrothermally treating the synthesis mixture at a temperature below 120°C for a time sufficient to effect formation of the zeolite.

2. A process as claimed in claim 1, wherein the structure directing agent is tetramethylammonium, tetraethylammonium, tetrapropylammonium, or tetrabutylammonium, hydroxide.

3. A process as claimed in claim 1, wherein the zeolite is an MFI, MEL, \*BEA, or OFF zeolite.

4. A process as claimed in any one of claims 1 to 3, wherein the synthesis mixture also contains an inorganic base.

5. A process as claimed in claim 4, wherein the base is potassium hydroxide.

6. A process as claimed in any one of claims 1 to 5, wherein the hydrothermal treatment is carried out at a temperature within the range of 40°C to 97°C.

7. A process for the manufacture of a colloidal suspension of Offretite, wherein a synthesis mixture having a molar composition, when calculated in terms of oxides, in the following ranges:

$K_2O:Al_2O_3$  0.25 to 0.5:1

$(TMA)_2O:Al_2O_3$  at least 2.0:1

$SiO_2:Al_2O_3$  8 to 10:1

$H_2O:Al_2O_3$  80 to 100:1.

wherein TMA represents the tetramethylammonium cation, is subjected to hydrothermal treatment at a temperature and for a time sufficient to form a colloidal suspension of Offretite.

8. A colloidal zeolite or colloidal zeolite suspension, whenever produced by the process of any one of claims 1 to 7.

9. The use of the product claimed in claim 8, if desired or required after washing, ion exchange, or calcining, in particulate or layer form, in hydrocarbon separations, conversions, or adsorptions.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 96/03098

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B39/04 C01B37/02 C01B39/48 C01B39/30 B01J29/06  
B01J29/035 B01J29/70 B01J29/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 130 809 (MOBIL OIL CORPORATION) 9 January 1985 see example 3 ---	1
A	WO,A,93 08125 (EXXON CHEMICAL PATENTS INC.) 29 April 1993 cited in the application see claim 4 ---	1
A	US,A,4 061 724 (R. W. GROSE ET AL.) 6 December 1977 ---	
A	US,A,3 578 398 (E. E. JENKINS) 11 May 1971 -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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19-11-96

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 96/03098

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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